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(71) Applicant: WITCO CORPORATION [US/US]; 520 Madison Avenue, New York, NY 10022 (US).

(72) Inventors: ROGERS, Jay, L. ; 37 Spindle Road, Hicksville, NY 11801 (US). AHLUWALIA, Surinder ; 2222 Settler Way Boulevard, Apt. 312, Sugarland, TX 77478 (US).

(74) Agents: ALEX, John, L. et al.; Lockwood, Alex, Fitzgibbon & Cummings, Three First National Plaza, Suite 1700, Chicago, IL 60602 (US).

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(54) Title: STABILIZER COMPOSITION AND POLYMER COMPOSITIONS STABILIZED THEREWITH

(57) Abstract

Methods of stabilizing a thermoplastic composition comprising a thermoplastic polymer and a fluorescent colorant against heat and processing degradation are disclosed. Compositions including a thermoplastic polymer, a fluorescent colorant and a conventional primary heat stabilizer and a stabilizer comprising a sodium perchlorate salt are disclosed. These compositions provide improved processing stability at processing temperatures of about 300 °F to about 400 °F.

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**STABILIZER COMPOSITION AND POLYMER
COMPOSITIONS STABILIZED THEREWITH**

Background of the Invention

The present invention relates to stabilizer compositions for fluorescent colorants and to plastic compositions containing fluorescent colorants having improved resistance to degradation to heat and processing at temperatures of about 300°F to about 400°F. More specifically, the present invention relates to the use of metal perchlorates, and in particular sodium perchlorates, to stabilize a thermoplastic composition comprising a thermoplastic polymer, a primary heat stabilizer and a fluorescent colorant against heat and processing degradation.

The problem of imparting to polyvinyl chloride a sufficient heat processing stability at temperatures at which the polymer becomes sufficiently fluid or softened to permit shaping is of course of long standing, and has been satisfactorily resolved by addition to the polymer of various combinations of known heat stabilizers. At these temperatures, the resin can degrade, liberating hydrogen chloride, and discolor, become brittle, and stick to the equipment. These problems are overcome by combining with the polymer before heat processing or during heat processing one or more of the well established and successful conventional heat stabilizers, such as, for example, the well known organotin stabilizers and/or metal salt stabilizers.

Although the well established and successful conventional heat stabilizers provide effective stabilization to the substrate polymer at elevated heat processing temperatures during standard processing, they may not provide effective stabilization to additives contained within the polymer during such heat processing. For example, although

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fluorescent colorants are used in a great many plastic products, their use is not without limitations. One important limitation is the sensitivity of fluorescent colorants to heat. When using fluorescent colorants, it is therefore desirable to keep the molding and extrusion temperatures and retention times to a minimum. Special heat-resistant fluorescent formulations will allow slightly higher processing temperatures and retention times. For instance, certain plastisol fluorescent formulations can withstand molding temperatures of 350°F-400°F for periods of from 5 to 10 minutes. These special heat-resistant formulations may, however, not be compatible with the desired end product substrate. Additionally, the heat sensitive aspect of fluorescent colorants, in general, and in such special formulations, limit their use in applications which involve longer processing times, and limit the ability to recycle scrap and spent articles containing fluorescent colorants.

Accordingly, a general object of the present invention is to provide a composition to stabilize a fluorescent colorant against heat and processing degradation.

It is another object of the present invention to provide a plastic composition containing a fluorescent colorant having improved processing stability at processing temperatures of about 300°F to about 400°F.

It is another object of the present invention to provide a method of stabilizing a thermoplastic composition comprising a thermoplastic polymer and a fluorescent colorant against heat and processing degradation.

It is another object of the present invention to provide novel stabilized thermoplastic compositions.

These and other objects of the present invention will be apparent to those skilled in the art from the following description.

Summary of th Invention

It has now been found that addition of a metal perchlorate, preferably sodium perchlorate, to a plastic

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composition containing a conventional heat stabilizer and fluorescent colorant provides improved heat and processing stability. In this regard, it has been found that sodium perchlorate has increased the longevity of fluorescence in a plastic composition containing a primary heat stabilizer and a fluorescent colorant. Improved resistance to heat and processing degradation of plastic compositions made of a thermoplastic polymer and a fluorescent colorant is obtained by combining with the thermoplastic polymer at least one conventional heat stabilizer and a sufficient amount of sodium perchlorate.

Detailed Description of the Invention

The thermoplastic polymers or resins which may be stabilized by practice of this invention include polystyrene, acrylonitrile-butadiene-styrene, polyamide, polycarbonate, polyacrylic, cellulose esters of carboxylic acids and halogen containing organic polymers. The cellulose esters of carboxylic acids include, for example, cellulose acetate, cellulose propionate, cellulose butyrate, and mixed esters such as cellulose acetate butyrate and cellulose acetate propionate. The halogen-containing organic polymers typically are those which contain chlorine atoms bonded to the polymer chain. These polymers may be homopolymers including polyvinyl chloride-type polymers, e.g. polyvinyl chloride. These polymers may also include copolymers formed by the copolymerization of vinyl chloride with other ethylenically unsaturated monomers. Ethylenically unsaturated monomers may be compounds which contain polymerizable carbon-to-carbon double bonds and may include alpha olefins such as ethylene, propylene and 1-hexene; acrylates, such as acrylic acid, ethyl acrylate, acrylonitrile; vinyl monomers, such as styrene, vinyl acetate; and/or maleates, such as maleic acid, maleic anhydride, maleic esters. For convenience, reference will be hereinafter made to vinyl chloride polymers.

The stabilizer combinations of this invention have applicability to both unplasticized or rigid polyvinyl

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chloride resins as well as plasticized polyvinyl chloride resins. The rigid polyvinyl chloride resins are defined as those containing at most about 10 percent plasticizer. Plasticized resins contain at least 10 percent plasticizer and can contain as much as 50 to 60 percent plasticizer according to the degree of plasticization desired. When plasticizers are to be employed, they may be incorporated into polyvinyl resins using conventional means. Conventional plasticizers can be used, such as dioctylphthalate, dioctyl adipate, dioctylsebacate and tricresyl phosphate. Additionally, it is possible to use epoxy plasticizers, polyester plasticizers, etc.

The fluorescent colorants incorporated within the plastic composition include, but are not limited to, fluorescent dyes and pigments. The fluorescent pigments include true pigments, i.e. an unextended inorganic or organic colorant insoluble in solvents of all kinds, and plastic carrier materials colored with fluorescent dyes, i.e. dyes and transparent synthetic resins which are finally ground to a desired particle size, e.g. particles in the range of 2 to 5 microns. These carrier materials can be thermoplastic or thermoset resins such as melamine formaldehyde, triazine formaldehyde, polyamide, polyester, and vinyl resins. It will be appreciated that a given carrier may be preferred for a given substrate plastic composition. Fluorescent colorants are commercially available from a number of sources such as Day-Glo Color Corp., a subsidiary of Nalco Chemical Company.

An effective amount of the fluorescent colorant is used. Typically, the higher the degree of clarity of the plastic, the greater the amount of fluorescent colorant needed to color the plastic. As with conventional pigments, fluorescent colorants are frequently prepared as concentrates and added in sufficient amount to achieve the desired final concentration in the plastic resin. Accordingly, the amount of colorant added will also depend upon the degree of concentration of the fluorescent colorant. Typically, fluorescent pigments are used in amounts ranging from 1 to 20

percent by weight of the plastic polymer.

The vinyl chloride polymers may also include other conventional additives and ingredients. These additives and ingredients include, but are not limited to, stabilizers impact modifiers, additional pigments and/or fillers, lubricants, etc. It will be appreciated that certain additives, especially other pigments and metal based stabilizers can affect the color and degree of fluorescence of the fluorescent colorant.

The preparation of the stabilized polymer composition is accomplished by conventional procedures. The selected stabilizer combination along with the desired compound and ingredients such as colorants, lubricants, antistatic agents, etc. as may be needed, is blended with the polymer being stabilized, using, for instance, plastic mixing rollers at a temperature at which the mix is fluid and thorough blending facilitated, typically at from 120° to 180°C for time sufficient to form a homogenous sheet, 5 minutes, usually. To facilitate incorporation of and reduce the amount of shear needed to incorporate a fluorescent pigment, it may be desirable to bring the plastic resin up to the minimum processing temperature of the carrier material of the fluorescent pigment prior to its addition. After the mass is formed, it is sheeted off in the usual way.

A sufficient amount of a conventional heat stabilizer or of a combination of conventional heat stabilizers is used to provide resistance to the polyvinyl resin from deterioration and physical properties during heat processing, including, for example, discoloration, reduction in melt viscosity and embrittlement. The conventional heat stabilizers include, but are not limited to conventional organo metallic stabilizers such as the known organotin carboxylates and mixtures thereof, and the known metal salts stabilizers such as barium salts, cadmium salts, calcium salts, zinc salts and mixtures thereof. The conventional stabilizers are normally used in an amount of 0.01 to 10 percent by weight of the resin and more preferably of

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conventional stabilizers are used in an amount of 0.1 to 5 percent by weight of the resin.

Specific examples of useful organotin stabilizers include alkyl mercaptides such as monomethyltin tris (isooctylthioglycolate), dimethyltin bis (isooctylthioglycolate), monomethyltin tris (2-ethylhexylthioglycolate), dimethyltin bis (2-ethylhexylthioglycolate), monobutyltin tris (isooctylthioglycolate), dibutyltin bis (isooctylthioglycolate), monobutyltin tris (2-ethylhexylthioglycolate), dibutyltin bis (2-ethylhexylthioglycolate), monomethyltin tris (mercaptoethyltallate), dimethyltin bis (mercaptoethyltallate), dibutyltin bis (mercaptoethyltallate), monobutyltin tris (mercaptoethyl laurate), dibutyltin bis (mercaptoethyl laurate), monomethyltin tris (isooctyl 3-mercaptoethylpropionate), dimethyltin bis (isooctyl 3-mercaptoethylpropionate), monobutyltin tris (isooctyl 3-mercaptoethylpropionate), dibutyltin bis (isooctyl 3-mercaptoethylpropionate), etc.; alkyltin sulfides such as monomethyltin sulfide, dimethyltin sulfide, monobutyltin sulfide, dibutyltin sulfide, etc.; alkyltin carboxylates such as dimethyltin dilaurate, dibutyltin dilaurate, dibutyltin dioctanoate, dibutyltin didecanoate, dibutyltin neodecanoate, dibutyltin dilaurate, dibutyltin ditallate, dioctyltin maleate, dibutyltin bis (dodecyl maleate), etc.; and mixtures thereof.

Specific examples of useful metal salt stabilizers include barium di(nonylphenolate), barium di(nonyl-o-cresolate), barium laurate, barium ricinoleate, barium myristate, barium benzoate, barium metatoluate, barium oxalate, barium malonate, barium laurate, barium tartrate, barium p-tert-butylbenzoate, barium succinate, barium glutarate, barium adipate, barium pimelate, barium suberate, barium azelate, barium sebacate, barium tallate etc., cadmium-2-ethylhexoate, cadmium laurate, cadmium stearate, cadmium naphthenate, cadmium benzoate, cadmium epoxystearate, cadmium myristate, cadmium p-tert-butylbenzoate, calcium stearate, calcium oxalate, calcium benzoate, zinc laurate, zinc oxalate,

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zinc malonate, zinc maleate, zinc tartrate, zinc benzoate, zinc metatoluate, zinc p-tert-butylbenzoate, zinc succinate, zinc adipate, zinc malate, zinc stearate, etc. Additionally, mixtures of the foregoing and/or other known metal salt stabilizers can be used.

In addition to the conventional heat stabilizers, there can also be added conventional antioxidants such as phenolic antioxidants normally used in an amount 0.01-10 percent, and more typically in an amount of 0.1 to 5 percent by weight of the weight of the conventional heat stabilizer. Additionally, conventional epoxy compounds such as epoxidized soy bean oil can be used in amounts of 0.01-10 percent by weight of the polymer.

In accordance with the present invention, in addition to the conventional heat stabilizer(s) and additives, a sufficient amount of a composition comprising a metal perchlorate salt is used to improve the resistance of the fluorescent colorant to heat and processing degradation. Preferably, the metal perchlorate salt is magnesium perchlorate; more preferably the metal perchlorate salt is lithium perchlorate, calcium perchlorate or barium perchlorate; and most preferably the metal perchlorate salt is sodium perchlorate.

The metal perchlorate stabilizer can be used in various forms such as an aqueous solution (approximately 60 percent or greater by weight metal perchlorate). Compositions also, optionally, can be prepared by combining a solution of metal perchlorate in water such as those commercially available from Ker-McGee Chemical Corporation, with calcium silicate such as the synthetic amorphous calcium silicate sold by the J.M. Huber Corporation under the trade designation Hubersorb 600 which has an average particle size according to the Coulter counter method of approximately 3.2 micrometers. It has been found that the use of calcium silicate in combination with the metal perchlorate solution does not adversely effect the stabilizing ability of the perchlorate and absorbs the water in the perchlorate solution to provide a

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perchlorate stabilizer composition which is relatively easy to handle and of reduced hazard level. Preferably, the metal perchlorate/calcium silicate combination also contains a non-absorbing diluent powder such as calcium carbonate to improve the composition's flowability. In this regard, calcium carbonate commercially available by Thomson Weinman Company under the trade name Atomite has been used. Other non-absorbing diluent powders include zeolites, silica, alumina, PVC resins, barium sulfate, and the like.

As noted, in practice, the metal perchlorate compositions are utilized in combination with a conventional heat stabilizer. In this regard, care should be exercised by the user to avoid potentially dangerous situations such as combining or otherwise directly contacting the perchlorate compositions with readily oxidizable compositions. From a hazard level aspect, conventional stabilizers susceptible to ready oxidation such as organic phosphites are not generally recommended for use with perchlorate compositions. When the perchlorate stabilizers of the present invention and compositions such as organic phosphites are both desired, it is best to add these components separately to the resin and exercise due care.

The amount of metal perchlorate used in the present invention is preferably from .001 to 5, and more preferably from .005 to 2 parts by weight of the weight of the plastic resin. To facilitate handling the metal perchlorate used in the present invention is preferably a metal perchlorate/calcium silicate composition comprising approximately 15 to 50 percent by weight of 60 percent aqueous metal perchlorate and approximately 50 to 85 percent by weight of calcium silicate. The amount of the metal perchlorate/calcium silicate composition used in the present invention is preferably from 0.1 to 10 parts, and more preferably from 0.5 to 5 parts by weight of the weight of the plastic resin.

The stabilizer systems of the invention including conventional heat stabilizers and metal perchlorate

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stabilizers can be compounded with polyvinyl chloride resins, properly formulated, and shaped by standard plastics processing techniques (including calendering, extrusion, injection and compression molding, blow molding, rotationally molding, slush and dip molding, solution casting, electrostatic spray and fluidized bed coating), to form a wide variety of components.

Compounding components such as plasticizers, lubricants, impact modifiers, processing aids, fillers, colorants, antistatic agents, tackifiers, flame retardants, fungicides, antiblocking agents, etc. can be incorporated to facilitate the processing of such components.

The following examples demonstrate the usefulness of the present invention.

EXAMPLES 1-6

Polyvinyl chloride resin compositions were prepared having the following base formulation:

<u>Ingredient</u>	<u>Parts By Weight</u>
Polyvinyl Chloride Homopolymer	100
Impact Modifier	15.5
Acrylic Process Aid	1.3
Acrylic Modifier	0.9
Lubricants	1.0
Baso Red 546 Fluorescent Dye	0.3
Primary Heat Processing Stabilizer (Composition comprising organic salts of barium and zinc, and an organic phosphite)	5

Depending upon the Example, the following components were added to the base formulation:

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<u>Example</u>	<u>Parts By Weight Addition To Base Formulation</u>
1	None
2	3.0 parts of a composition comprising 40 weight percent calcium silicate, 45 percent calcium carbonate, and 15 weight percent of 60% aqueous sodium perchlorate solution
3	3.0 parts of a composition comprising 40 weight percent calcium silicate, 45 weight percent calcium carbonate and 15 weight percent of 60% aqueous lithium perchlorate solution;
4	3.0 parts of a composition comprising 40 weight percent calcium silicate, 45 weight percent calcium carbonate and 15 weight percent of 60% aqueous calcium perchlorate solution;
5	3.0 parts of a composition comprising 40 weight percent calcium silicate, 45 weight percent calcium carbonate and 15 weight percent of 60% aqueous magnesium perchlorate solution;
6	3.0 parts of a composition comprising 40 weight percent calcium silicate, 45 weight percent calcium carbonate and 15 weight percent of 60% barium perchlorate solution;

EXAMPLES 7-12

Polyvinyl chloride resin compositions were prepared having the following base formulation:

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<u>Ingredient</u>	<u>Parts By Weight</u>
Polyvinyl Chloride Homopolymer	100
Impact Modifier	15.5
<u>Ingredient</u>	<u>Parts By Weight</u>
Acrylic Process Aid	1.3
Acrylic Modifier	0.9
Lubricants	1.0
Baso Red 546 Fluorescent Dye	0.3
Primary Heat Processing Stabilizer (methyltin isooctylthioglycolate mixture of approximately 20 percent monomethyltin tri isooctylthiogly- colate and 80 percent dimethyltin bis isooctylthioglycolate)	1.5

<u>Example</u>	<u>Parts By Weight Addition To Base Formulation</u>
7	None
8	3.0 parts of a composition comprising 40 weight percent calcium silicate, 45 percent calcium carbonate, and 15 weight percent of 60% aqueous sodium perchlorate solution
9	3.0 parts of a composition comprising 40 weight percent calcium silicate, 45 weight percent calcium carbonate and 15 weight percent of 60% aqueous lithium perchlorate solution;
10	3.0 parts of a composition comprising 40 weight percent calcium silicate, 45 weight percent calcium carbonate and 15 w ight percent of 60% aqu ous calcium perchlorate solution;

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<u>Example</u>	<u>Parts By Weight Addition To Base Formulation</u>
11	3.0 parts of a composition comprising 40 weight percent calcium silicate, 45 weight percent calcium carbonate and 15 weight percent of 60% aqueous magnesium perchlorate solution;
12	3.0 parts of a composition comprising 40 weight percent calcium silicate, 45 weight percent calcium carbonate and 15 weight percent of 60% barium perchlorate solution;

The formulations of Examples 1-12 were blended on a two-roll mill, and then sheeted off. To determine heat processing stability, samples of Examples 1-12 were cut from the sheet and heated in an oven at 350°F for up to 80 minutes and at 375°F for up to 40 minutes. Samples were withdrawn at 10 minute and 5 minute intervals, respectively, to follow the progress of any deterioration, as evidenced by visible discoloration.

The sample of Example 1, the control, subjected to the oven test at 350°F, at 20 minutes was visibly degraded, i.e. black. At 350°F, samples from Examples 2-6 showed relatively little visible difference in discoloration from the unexposed sample through 40 minutes. At 50 minutes, samples of Examples 5 and 6 were visibly worse, i.e. had dark spots, then were samples of Examples 2-4. At 60 minutes, samples of Examples 5 and 6 were visibly degraded; and samples of Examples 3 and 4 had dark spots like Examples 5 and 6 had at 50 minutes; the sample of Example 2 had little or no degradation and was visibly better than the samples Examples 3 and 4 were at 60 minutes. At 70 minutes, the samples of Examples 3-6 were visibly degraded, i.e. black; and the samples of Example 2 had dark spots similar to but not as bad as those of the samples of Examples 3 and 4 at 60 minutes. At

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70 minutes, the sample of Example 2 had visibly degraded.

The sample of Example 1 subjected to the oven test at 375°F showed relatively little visible difference at 5 minutes but was visibly degraded, i.e. black, at 10 minutes. At 375°F, samples of Examples 2-6 showed little visible difference through 15 minutes. At 20 minutes, samples of Examples 5 and 6 were visibly worse, i.e. had dark spots, than were samples of Examples 2-4. At 25 minutes, the samples of Examples 4, 5 and 6 were visibly degraded, i.e. black, and Example 3 had visibly worsened in appearance to the appearance the sample of Example 5 had exhibited at 20 minutes. At 30 minutes, the samples of Examples 2 and 3 were visibly degraded, i.e. black.

The samples of Example 7 subjected to the oven test at 350°F were visibly worse in discoloration from the unexposed sample at 10 minutes, i.e. uniformly darkly discolored, and were visibly degraded, i.e. black at 20 minutes. The samples of Examples 8-12 subjected to the oven test at 350°F showed relatively little visible difference in discoloration from the unexposed sample throughout the 80 minutes of the test.

The sample of Example 7 subjected to the oven test at 375°F was visibly degraded, i.e. black, at 5 minutes. The samples of Examples 8-12 subjected to the oven test at 375°F showed relatively little visible difference in discoloration from the unexposed sample through 20 minutes. At 25 minutes, the samples from Examples 8-12 were visibly worse, i.e. were darker, than before. The samples of Examples 8-12 became progressively further discolored at 30, 35 and 40 minutes but even at 40 minutes the samples of Examples 8-12 were visibly better, i.e. had not turned black, than the sample of Example 7 at 5 minutes.

EXAMPLES 13-33

<u>Ingredient</u>	<u>Parts By Weight</u>
Polyvinyl Chloride Homopolymer	100
Phthalate Plasticizer	28

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EXAMPLES 13-33 CONT.

<u>Ingredient</u>	<u>Parts By Weight</u>
Adipate Plasticizer	11
Epoxide Stabilizer	15
Primary Heat Processing Stabilizer (composition comprising organic salts of zinc and barium and organics solvents)	4

Depending upon the Example, the following components were added to the base formulation:

<u>Example</u>	<u>Colorant Added at 10 Parts by Weight</u>	<u>Parts by Weight Addition To Base Formulation</u>
13	Red Neon	None
14	Red Neon	1.0 parts of a composition comprising 35 weight percent calcium silicate, 50 weight percent calcium carbonate and 15 weight percent of 60% aqueous sodium perchlorate solution
15	Red Neon	0.15 parts of 60 percent aqueous sodium perchlorate solution
16	Red Neon	3.0 parts of a composition comprising 35 weight percent calcium silicate, 50 weight percent calcium carbonate and 15 weight percent of 60% aqueous sodium perchlorate solution
17	Red Neon	0.45 parts of 60% aqueous sodium perchlorate solution
18	Red Neon	5.0 parts of a composition comprising 35 weight percent calcium silicate, 50 weight percent calcium carbonate and 15 weight\

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<u>Exempl</u>	<u>Colorant Added at 10 Parts by Weight</u>	<u>Parts by Weight Addition To Base Formulation</u>
		percent of 60% aqueous sodium perchlorate solution
19	Red Neon	0.75 parts of 60% aqueous sodium perchlorate solution
20	Saturn Yellow	None
21	Saturn Yellow	1.0 parts of a composition comprising 35 weight percent calcium silicate, 50 weight percent calcium carbonate and 15 weight percent of 60% aqueous sodium perchlorate solution
22	Saturn Yellow	0.15 parts of 60 percent aqueous sodium perchlorate solution
23	Saturn Yellow	3.0 parts of a composition comprising 35 weight percent calcium silicate, 50 weight percent calcium carbonate and 15 weight percent of 60% aqueous sodium perchlorate solution
24	Saturn Yellow	0.45 parts of 60% aqueous sodium perchlorate solution
25	Saturn Yellow	5.0 parts of a composition comprising 35 weight percent calcium silicate, 50 weight percent calcium carbonate and 15 weight percent of 60% aqueous sodium perchlorate solution
26	Saturn Yellow	0.75 parts of 60% aqueous sodium perchlorate solution
27	Signal Green	None
28	Signal Gr en	1.0 parts of a composition comprising 35 weight

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<u>Example</u>	<u>Colorant Added at 10 Parts by Weight</u>	<u>Parts by Weight Addition To Base Formulation</u>
		percent calcium silicate, 50 weight percent calcium carbonate and 15 weight percent of 60% aqueous sodium perchlorate solution
29	Signal Green	0.15 parts of 60 percent aqueous sodium perchlorate solution
30	Signal Green	3.0 parts of a composition comprising 35 weight percent calcium silicate, 50 weight percent calcium carbonate and 15 weight percent of 60% aqueous sodium perchlorate solution
31	Signal Green	0.45 parts of 60% aqueous sodium perchlorate solution
32	Signal Green	5.0 parts of a composition comprising 35 weight percent calcium silicate, 50 weight percent calcium carbonate and 15 weight percent of 60% aqueous sodium perchlorate solution
33	Signal Green	0.75 parts of 60% aqueous sodium perchlorate solution

The formulations of Examples 13-33 were mixed at room temperature to give flowable paste dispersions of the PVC resin in the liquid ingredients, briefly held under vacuum to remove air bubbles, drawn down on glass plates and fused for three minutes in a circulating air oven at 400°F (205°C). Samples of the resulting flexible plastic sheets were further exposed in a 400°F oven and removed at 2 minute intervals to follow the progress of heat-induced changes to the formulation. The removed samples were exposed to ultraviolet

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black-light and visually observed to determine whether the samples still evidenced fluorescence. The following Table 1 shows for each Example the number of minutes at 400°F that the fluorescence remains visible under ultraviolet black-light.

TABLE 1

<u>EXAMPLE</u>	<u>MINUTES</u>
13	6-8
14	14-16
15	>18
16	>18
17	>18
18	>18
19	>18
20	12-14
21	14
22	16
23	>18
24	>18
25	>18
26	>18
27	14
28	18
29	>18
30	>18
31	>18
32	>18
33	>18

EXAMPLE 34-50IngredientParts By Weight

Polyvinyl Chloride Homopolymer

100

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EXAMPLE 34-50 CONT.

<u>Ingredient</u>	<u>Parts By Weight</u>
Impact Modifier	15
Acrylic Process Aid	1.5
Lubricants	2
Ultraviolet Absorber Stabilizer	1.0
Baso Red 546 Fluorescent Dye	0.25

Depending upon the Example, the following components were added to the base formulation:

<u>Example</u>	<u>Parts by Weight Stabilizer</u>	<u>Parts By Weight Of A Composition Composition Comprising 35 Weight Percent Calcium Silicate, 50 Weight Percent Calcium Primary Heat and 15 Weight Percent of 60% Aqueous Sodium Perchlorate Solution</u>
34	3.0 parts dibutyltin maleate	None
35	3.0 parts dibutyltin maleate	1.0
36	3.0 parts dibutyltin maleate	2.0
37	3.0 parts of a composition comprising organic salts of zinc and barium and organic solvents	None
38	3.0 parts of stabilizer of Example 37	2.0
39	5.0 parts of stabilizer of Example 37	None
40	5.0 parts of stabilizer of Example 37	2.0
41	3.0 parts of a composition comprising organic salts of calcium and zinc, an organic phosphite and an organic solvent	None
42	3.0 parts of stabilizer of Example 41	2.0
43	5.0 parts of stabilizer of Example 41	None
44	5.0 parts of stabilizer of	2.0

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Example 41

45	3.0 parts of composition comprising organic salts of zinc, cadmium and barium, phosphites and an organic diluent	None
46	3.0 parts of stabilizer of Example 45	2.0
47	3.0 parts of a composition comprising organic salts of zinc and barium, an organic phosphite and an organic diluent	None
48	3.0 parts of a stabilizer of Example 47	2.0
49	5 parts of stabilizer of Example 47	None
50	5 parts of stabilizer of Example 47	2.0

Formulations of Examples 34-50 were blended on a two-roll mill, and then sheeted off to determine heat processing stability, samples of Examples 34-50 were cut from the sheet and heated in an oven at 350°F and at 375°F for up to 80 minutes. Samples were withdrawn at 10 minute intervals to follow the progress of any deterioration, as evidenced by visible discoloration and/or absence of fluorescence when exposed to ultraviolet black-light.

Visual inspection of Examples 34-50 subjected to the oven test at 350°F indicated that, in general, the addition of the sodium perchlorate solution extended the time before visible degradation was apparent. For instance, samples of Example 34 compared to the unexposed sample evidenced a noticeable color change by 20 minutes and were visibly degraded, i.e. black, by 30 minutes; whereas, samples of Examples 35 at 80 minutes had yet to turn black but had degraded to the appearance of the sample of Example 34 at 20

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minutes. The samples of Example 36 showed relatively little visible difference from the unexposed sample through 70 minutes and at 80 minutes had a similar appearance to the appearance of the sample of Example 34 at 20 minutes. The samples of Examples 37, 39, 45 and 47, compared to the respective unexposed samples were visibly degraded by 10 minutes; whereas, samples of Examples 38, 40, 46 and 48, did not appear visibly degraded to the same degree as the 10 minute samples of Examples 37, 39, 45 and 47, respectively, until 30 minutes.

Compared to the respective unexposed sample, the sample of Example 41 was visibly degraded by 10 minutes; whereas, the sample of Exhibit 42 had not visibly degraded until 20 minutes. At 10 minutes the sample of Exhibit 43 was visibly worse, i.e. had numerous dark spots, than was the sample of Example 44 at 10 minutes. The samples of Exhibit 49 were visibly degraded by 20 minutes whereas the samples of Exhibit 50 were not visibly degraded until 30 minutes.

Table 2 below reflects the number of minutes that fluorescence remained visible under ultraviolet black-light for samples of Examples 34-50 subjected to 375°F:

TABLE 2

<u>EXAMPLE</u>	<u>MINUTES</u>
34	20
35	20
36	>80
37	10
38	20
39	10
40	20

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41	10
42	20
43	10
44	20
45	10
46	20
47	<10
48	between 20 and 30
49	10
50	between 20 and 30

EXAMPLES 51-53

Cellulose acetate resin compositions were prepared having the following base formulation:

<u>Ingredients</u>	<u>Parts By Weight</u>
Cellulose Acetate Powder	100.00
Phthalate Plasticizer	39.00
Acid Acceptor	0.02
Antioxidant	0.4
R-99 Rhodamine Dye (Orange)	0.10
Phosphite Stabilizer	0.07
Epoxide Stabilizer	0.60

Examples 51-53 comprise the base formulation and 0.15 parts, 0.20 parts and 0.25 parts, respectively, of a composition comprising 70 weight percent calcium silicate and 30 weight percent of 60% aqueous sodium perchlorate solution. It is believed that, of Examples 51-53, Example 52, i.e. 0.20 parts added perchlorate stabilizer composition, would provide the best color-hold formulation for normal processing temperatures. It is also believed that, in general, the formulations of Examples 51-53 would provide a ten (10) minute extension of color-holding properties during normal processing temperatures compared to the formulation of the base

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formulation, i.e. formulations without the sodium perchlorate stabilizer composition.

The foregoing Examples 1-53 demonstrate that when a sodium perchlorate salt is incorporated into thermoplastic compositions containing a primary heat stabilizer and a fluorescent colorant the composition, and in particular the fluorescent colorant, exhibits improved heat and processing stability compared to similar compositions without a perchlorate component.

WHAT IS CLAIMED IS:

1. A plastic composition which comprises a thermoplastic polymer, a fluorescent colorant and a stabilizer increasing the longevity of fluorescence of said fluorescent colorant consisting essentially of a sodium perchlorate salt.

2. The composition of claim 1 wherein said stabilizer is present in an amount of from about 0.1 to about 2 weight percent to the weight of said thermoplastic polymer.

3. The composition of claim 1 wherein said thermoplastic polymer is selected from the group consisting of polystyrene, acrylonitrile-butadiene-styrene, polyamide, polycarbonate, polyacrylic, cellulose esters of carboxylic acids and polyvinylchloride thermoplastic polymers and combinations thereof.

4. The composition of claim 1 wherein said thermoplastic polymer comprises polyvinylchloride.

5. The composition of claim 1 wherein said thermoplastic polymer comprises cellulose acetate.

6. The composition of claim 1 wherein said fluorescent colorant is a fluorescent pigment.

7. The composition of claim 6 wherein said fluorescent pigment comprises a fluorescent colorant and a thermoplastic carrier material.

8. The composition of claim 1 wherein said fluorescent colorant is a fluorescent dye.

9. The composition of claim 1 wherein said stabilizer further comprises calcium silicate.

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10. A plastic composition which comprises a thermoplastic resin, an effective amount of a primary heat stabilizer composition to provide processing stability at processing temperatures of about 300°F. to about 400°F. to said thermoplastic resin, a fluorescent colorant, and an effective amount of a secondary heat stabilizer composition to increase the longevity of fluorescence of said fluorescent colorant during such processing temperatures, said secondary stabilizer composition consisting essentially of a sodium perchlorate salt.

11. The composition of claim 10 wherein said primary heat stabilizer is selected from the group consisting of organotin stabilizers and metal salt stabilizes.

12. The composition of claim 10 wherein said organotin stabilizers comprise organotin mercaptides, organotin sulfides, organotin carboxylates and mixtures thereof.

13. The composition is claim 12 wherein said primary heat stabilizer is dibutyltin maleate.

14. The composition of claim 10 wherein said metal salt stabilizers comprises barium salts, cadmium salts, calcium salts, zinc salts and mixtures thereof.

15. The composition of claim 10 wherein said secondary stabilizer is present in an amount of from about 0.1 to about 2 weight percent to the weight of said thermoplastic polymer.

16. The composition of claim 10 wher in said thermoplastic polymer is selected from the group consisting of

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polystyrene, acrylonitrile-butadiene-styrene, polyamide, polycarbonate, polyacrylic, cellulose esters of carboxylic acids and polyvinylchloride thermoplastic polymers and combinations thereof.

17. The composition of claim 10 wherein said thermoplastic polymer comprises polyvinylchloride, and said fluorescent colorant is selected from the group consisting of fluorescent pigments, fluorescent dyes and combinations thereof.

18. A method for stabilizing a thermoplastic composition comprising a thermoplastic polymer and a fluorescent colorant against heat and processing degradation said method comprising incorporating within said composition a primary heat stabilizer for such thermoplastic resin and a secondary stabilizer increasing the longevity of fluorescence of said fluorescent colorant said secondary stabilizer consisting essentially of a sodium perchlorate salt.

19. The method of claim 18 wherein said primary heat stabilizer is selected from the group consisting of organotin stabilizers and metal salt stabilizes.

20. The method of claim 18 wherein said organotin stabilizers comprise organotin mercaptides, organotin sulfides, organotin carboxylates and mixtures thereof.

21. The method is claim 18 wherein said primary heat stabilizer is dibutyltin maleate.

22. The method of claim 18 wherein said metal salt stabilizers comprises barium salts, cadmium salts, calcium salts, zinc salts and mixtures thereof.

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23. The method of claim 18 wherein said secondary stabilizer is present in an amount of from about 0.1 to about 2 weight percent to the weight of said thermoplastic polymer.

24. The method of claim 18 wherein said thermoplastic polymer is selected from the group consisting of polystyrene, acrylonitrile-butadiene-styrene, polyamide, polycarbonate, polyacrylic, cellulose esters of carboxylic acids and polyvinylchloride thermoplastic polymers and combinations thereof.

25. The method of claim 18 wherein said fluorescent colorant is selected from the group consisting of fluorescent pigments, fluorescent dyes and combinations thereof.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US92/06149

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) : C 08K 5/15

US, A, 4810078 (Armstrong) 07 March 1989, cols. 3-9

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 252/301.33, 301.34, 301.35; 549/227

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP, A, 62-36446 (KYODD YA KUHIN KOGYO K.K.) 17 February 1987. See Chemical Abstracts citation proceeding.	1-25
	Chemical abstracts, volume 107, article citation No. 107: 199559r, (1987), (KYODO YAKUHIN KOGYO K.K.).	1-25
Y	JP, A, 53-11948 (ADEKA ARGUS-CHEMICAL CO. LTD.) 02 FEBRUARY 1978, SEE PROCEEDING CHEMICAL ABSTRACTS CITATION.	1-25
	CHEMICAL ABSTRACTS, VOLUME 89, ARTICLE CITATION NO. 89:711Lh (1978), (ADEKA ARGUS CHEMICAL CO., LTD.)	
	US, A, 4,442,017 (BLUMBERG ET AL) 10 APRIL 1984, COL. 1, LINE 46 - COL. 2, LINE 36, COL. 4, LINES 36-45 AND THE EXAMPLES:	1-25

☐ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	*T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be part of particular relevance	*X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
E earlier document published on or after the international filing date	*Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Z*	document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means		
P document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

15 SEPTEMBER 1992

Date of mailing of the international search report

18 NOV 1992

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 Box PCT
 Washington, D.C. 20231

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Authorized officer

VERONICA P. HOKE

Telephone No. (703) 308-2351

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US92/06149

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US,A,4,675,356 (MIYATA) 23 June 1987, col. 9 lines 39-40 and col.10, lines 3-11	1-25
Y	US,A,1,645,451 (RABE ET AL) 11 October 1927, Example 1 and Col. two, lines 5-9	1-25
Y	SU,A, 952,925 (ALEKSEEVA VI) 11 April 1980 See accompanying Derwent Abstract	1-25